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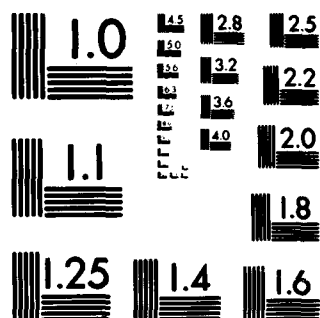
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BRASS CARTRIDGE CASE FLAW DETECTION

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) It appeared in earlier work at Frankford Arsenal that an improperly annealed condition in small caliber cartridge cases could be detected by thermal imaging with liquid crystals. If applicable, this could be used to replace the "Mercury Cracking Test" (based on ASTM Method B 154-58, Mercurous Nitrate Test for Copper and Copper Alloys). This would allow eliminating mercury and spent acid from the effluent from cartridge case production lines.		

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1. INTRODUCTION

The objective of this program was to ascertain the feasibility of determining residual stresses in small caliber cartridge cases caused by improper annealing during fabrication. These stressed areas are a source of incipient cartridge case failure, resulting in debulleting or failure of the case to seal the chamber. The method currently used is the ASTM B 154-58 (1965) "Mercurous Nitrate Test for Copper and Copper Alloys." Although a good quality control procedure, its use involves the disposition of quantities of spent nitric acid, mercurous nitrate solutions, and elemental mercury. The U.S. Army, seeking to eliminate this source of polluting effluent from its plants, investigated the use of thermal imaging with liquid crystals (LC) as a "stress indicator" at Frankford Arsenal in a program conducted by Dr. J. Radell. This methodology seemed capable of imaging stress in flat copper sheets and in small caliber cartridge cases. The effort, however, centered more on devising liquid crystal formulations, case cleaning, and coating techniques than on answering several important questions:

- Is the observed effect really "imaging" the stresses in the metal or is some artifact of the specimen or method being observed?
- How well could the "yes/no" answers of such a test be expected to correlate with the presence/absence of residual stress in a cartridge case?

Accordingly, this program was undertaken to answer these questions. The source of LC was limited to those used in thermography and thus commercially available. The evaluation was to be conducted on a comparative basis by observing the behavior of LC coated on cartridge cases known to be properly annealed (A) and on sample cases purposely not stress relieved, that is, not annealed (NA).

The following test was proposed:

A cleaned cartridge case would be painted with a thin black undercoating, dried, and then coated with a LC paint. The specimen would be placed on a hot plate, base down. LC can be made to display a characteristic color change, associated with a "phase change" over a narrow temperature range, typically 2-3°C. Thus, as the outer surface of the cartridge case passed through this temperature range, the color of the LC would change. A ring of color was observed to progress from the base of the case to the mouth. It was suggested that stressed areas would conduct heat differently than unstressed areas and hence would show a difference in the progression of color bands. This method was similarly used to indicate areas of poor bonding between the sub-surface structure and the skin of helicopter blades.

The program was supplied with samples of cartridge cases in various stages of manufacture. The first attempts to run tests on these samples were confounded due to uncertainty in the designation of the received samples. Before this problem could be resolved Frankford Arsenal was deactivated. The program suffered a hiatus until late in 1977. Dr. James Mikula at the Army Armaments Research and Development Command (ARRADCOM) was then assigned the responsibility for this program. Recognizing that the ability to proceed was dependent on a certifiable source of "good" and "bad" cases, Dr. Mikula made arrangement for such samples.

In January of this year the author and Dr. Mikula visited Lake City Army Ammunition Plant (LCAAP), to observe case manufacturing and testing procedures. A sample of 100 each of A and NA 5.56 mm cartridge cases were obtained. These samples were the basis for the work described in this report. It was demonstrated at LCAPP that 5 out of 5 NA cartridge cases failed the "mercury cracking test," while all A cases passed the test.

2. DISCUSSION

2.1 Mercury Cracking Test

This procedure has been used extensively for evaluating the annealing of the mouth of small caliber cartridge cases for many years. It is based on ASTM B 154-58 (1965) "Mercurous Nitrate Test for Copper and Copper Alloys." A copy of this procedure is appended to this report.

Sample cartridge cases are withdrawn from the production line according to a quality assurance plan. The primer pockets are formed but not drilled. The cases are brought to the laboratory and an appropriate bullet pressed into the case to stress the neck area. The assembly is then immersed in the dilute nitric acid cleaning solution until the cases are etched to a uniform color. The cases are rinsed with fresh water and then covered with the mercurous nitrate solution for 15 minutes. (During this period, cracks can be properly observed in the neck portion of cases which have not been properly annealed.) At the end of this time the cases are again rinsed with water. Slight pressure against the bullet in those specimens which were improperly or not annealed results in the complete failure of the case neck.

This is shown in Figure 1. Properly annealed cases do not fail in this manner. This was observed at LCAAP and was repeated in our laboratory on the samples from Lake City. (Drops of elemental mercury can be seen on the surface of the cases in the photograph.)

2.2 Liquid Crystals

A detailed discussion of the theoretical aspects of liquid crystals (LC) is beyond the scope of this program. The types of LC of interest in this effort are designated as cholesteric. These materials generally, as the name implies, are esters of cholesterol. In the LC form the overall arrangement consists of layers: within each layer the molecules are considered to



Figure 1

Results of Mercurous Nitrate Test On
Annealed (Right) and Not Annealed (Left) Cartridge Cases

lie flat and parallel to each other. The orientation of the molecules rotates from layer to layer in a prescribed structural manner. This structure exhibits unusual optical properties along the axis normal to the surface of the LC.

Particularly interesting is the ability of LC to reflect light selectively across specific ranges of temperature. Illuminated with direct lighting, thin layers of cholesteric LC appear to be colored, the reflected color being strongly dependent on the temperature of the film.

Each compound has a specified melting point at which the effect starts and a span of temperature over which this effect can occur: typically 1 to 3 degrees. At temperatures lower and higher than this range the film is colorless. At the low end of the active range the film turns red. As the temperature of the film is increased, the whole color spectrum, through violet at the upper end of the temperature range, can be observed. Beyond this point the film is again colorless.

This process is reversible: crossing the temperature range from the upper limit one would observe violet thru red transitions.

These colors are not intrinsic colors of the crystals but are the light reflected by the highly ordered structure. In order to keep the light which is not reflected by the LC from being reflected by the supporting substrate, it must be non-reflective. This is achieved by coloring it a dull black.

The selective light reflection of these materials can be also affected by pressure, magnetic and electrical fields, and chemical agents.

Utilizing this responsiveness to temperature, LC have found application in non-destructive testing of electronic circuits, of actively stressed mechanical components such as springs, of heat flow in heat transfer systems, and in medical

applications where variations in skin temperature are indicative of pathological differences.

There are also examples where the flow of heat from an applied source can be used to display discontinuities in the system, e.g., the non-destructive testing of adhesively bonded panels, flaws in honeycomb structures, visualization of cavities and cracks. This apparently led to the concept of thermally visualizing residual stresses in small caliber brass cartridge cases.

2.3 Proposed Method

The concept uses LC to display thermographically a difference in surface temperature due to the annealed/unannealed condition of a brass cartridge case. It was proposed that the base of the cartridge case be placed against a heated surface with a large thermal capacity, such as a hot plate. Isotherms could then travel up the length of the case until it was in thermal equilibrium with the heat source. The cartridge case would be coated with a LC thermal indicator whose active temperature range would display the isotherms generated by the flow of heat from the hot plate.

If, for example, the case were coated with a LC having a temperature indicating range of 31 to 33°C and then placed on a hot plate with a surface temperature of 50°C, a red band, corresponding to 31°C would be observed to travel up the cartridge case. Behind this band would follow a $\frac{1}{2}$ -inch-wide band of colors, through the rest of the spectrum to violet (33°C).

It was suggested that A and NA stressed brass would behave differently in this test, implying that these two different crystallographic forms of brass have different heat capacities and/or thermal resistance. (The temperature of the surface of the cartridge case at a given point and time, treated in the above fashion, would be a function of these intrinsic properties

of the brass). A literature search failed to yield information about this subject. Intuitively one expects that these properties would be only marginally different for the two crystal structures. Yet the Frankford Arsenal work indicated that there was a difference. The question then was whether or not the effect was an artifact of the experiment or associated with the metallurgy of the specimen.

2.4 Experimental Approach

The above question might best be answered by developing a method that would make the LC display small differences in the surface temperature of brass cartridge cases. A statistically significant number of cases, known to be either A or NA, could then be tested. The level of confidence in the test procedure could then be expressed and compared to the standard "mercury cracking test." This first order evaluation would indicate the merit of continuing development.

Several problem areas were recognized. Coating the brass substrate black in order to view the reflected color of liquid crystals could affect the sensitivity of the procedure. In general, paints or thin coatings were used. The temperature of the LC had to be raised to a specified value in order to display its characteristic color. This was accomplished by the transfer of heat from the brass substrate. The black coating, however, could only impede the flow of heat, i.e., damp the response. Even worse, the effect would be a function of thickness, the variability being related to the ability to apply reproducibly thin and uniform coatings. This requirement served to complicate the proposed method.

In view of the above it seemed worthwhile to examine the possibility of chemically blackening the brass instead of applying a coating. Several procedures were found and tried.

The application of LC posed similar problems. At Frankford Arsenal the coatings were applied by brush. The preferred method of application undoubtedly would be by spray application. The limited resources available to this program did not permit extensive experimentation with spray formulations; a cursory investigation of this problem was carried out with little success. Accordingly, the LC investigated were used in the form available, two by painting and two by spray-coating from aerosol cans.

The experimental details and the results obtained are described in the following sections.

3. EXPERIMENTAL DETAILS

3.1 Preliminary Tests

Preliminary tests to develop methods for case blackening or undercoating, application of the LC's, choice of LC and heating rates were carried out using cartridge cases supplied by Frankford Arsenal. The source and state of anneal of these cases and cases in various stages of drawing were uncertain. They were, however, suitable for the purpose of developing the techniques described below.

3.1.1 Case blackening

It was believed that the use of black paint as a base, necessary to view the reflected LC colors, dampens the response of the LC to the brass temperature.

Two chemical methods of blackening the brass were tried. An acid cleaning solution of:

Sulfuric Acid	62% (vol)
Nitric Acid	31%
Water	7%
HCl	1 oz/gal

was used to remove any oxide from the brass. The cases were rinsed in water and immersed in one of two blackening solutions.

Solution A consisted of:

Sodium Thiosulfate	25 g
Lead Acetate	25 g
Water	1 liter

Solution B consisted of:

Copper Carbonate	120 g
Ammonium hydroxide	250 ml
Water	750 ml

The brass was immersed in either solution at about 70-80°C, just long enough to blacken.

Neither method provided a deep enough "black" to be useful for viewing the LC changes. When coated with the LC the black appearance was mottled and tended to appear gray. This effort was abandoned with the option to reexamine the procedure if the results of the LC test so warranted.

In an alternative scheme, a coating of "India Ink"¹ looked very good but was quite fragile. LC had to be applied by either spraying or dipping, as the India Ink undercoating could not stand brush application.

An alcohol-based black paint² applied from an aerosol spray can and specifically designed for use with LC in a medical procedure was not useful, as the coating crazed on drying on the brass surface.

The preferred method consisted of degreasing the cartridge case by dipping in Freon 113³ several times and allowing the solvent to evaporate. The cartridge case was then placed on a mandrel, neck down, mounted in a slow speed stirring motor

¹Pelikan Drawing Ink #17. Obtainable in art supply stores. Any "India Ink" will suffice.

²Lix Kit Black Undercoat - Fisher Scientific Catalogue No. 6-650.

³Freon is available from E. I. DuPont.

turning at several hundred rpm. A very light spray coat of Krylon Ultra Flat Black 1602⁴ was applied from an aerosol spray can. The coating was dried in a flow of warm air and another light coat of paint applied. This was repeated until the entire case appeared to be uniformly coated. With experience it was possible to apply a uniform coat on a 5.56 mm case with 35 to 50 mg of paint. Finer control than this would require automated equipment.

3.1.2 Liquid Crystal Application

We had initially acquired from Eastman⁵ a series of LC - cholesteryl esters varying in melting points from about 70 to 150°C. The two chosen, cholesteryl propionate and nononate, were pure semi-solids made into 10% solutions (wt) in petroleum ether. They had to be applied by brush or by dipping. Since uniform application was difficult and equivalent materials already formulated for spray application were available, the Eastman materials were not considered further.

Another source of LC was the LIX KIT "Thermographic Spray Kit" by Liquid Crystal Biosystems Inc., available from Fisher Scientific (catalogue number 6-650) in aerosol spray cans in 70% ethyl alcohol. The transition ranges (red thru violet) available were 30-33°C, 31-34°C, 32-35°C, and 33-36°C.

LC could also be obtained from:

Djinni Industries Inc.
1776 E. First St.
Dayton, Ohio 45403

in the form of water-based encapsulated LC (ELC) which had to be applied by brush. Color transition temperature spans of 2°C starting at 22, 24, 26, 28, 30, 33°C were available.

⁴Borden Inc., Dept. CP, Columbus OH 43215.

⁵Eastman, Rochester, N.Y. 14650.

Djinni also produced an oil-based solution applied from spray cans. Two were purchased: 30-33°C and 33-36°C, the temperature span for the red to violet change.

Considering all the temperature ranges available, only those with initial color changes above 28°C were considered useful since ambient temperatures are only a few degrees lower. LC having color transition temperatures within the expected range of ambient temperatures would not be useful.

After considerable effort to develop procedures for the application of the LC, the following conclusions were drawn.

The water-based ELC, when diluted to a sprayable consistency for an artist's air brush, contained so little solid that consistently uniform coating was impossible. The water base also made drying of the cases between coats difficult. A mixture of 1 part (vol) of water to 2 parts of the ELC slurry could be applied in multiple coats with a small camel hair brush. Air drying between coats was required. Coating uniformity and reproducibility left something to be desired. Spray application was thus preferred.

Two spray formulations were available. LIX KIT, alcohol-based, and the Djinni LC, oil-based. Both formulations provided uniform coatings. The minimum useful coating weights varied between 35 to 60 mg for a 5.56 mm cartridge case.

The cartridge case was rotated before the spray nozzle in the same manner as when applying the black undercoating. The spray can was held a uniform distance, about 10 in. away from the rotating specimen. Only a small amount of material was applied at any one time and drying was allowed between coats.

The oil-based spray gave a smooth, shiny finish, compared to the LIX spray or the formulations applied by brush. This high-gloss finish made the color rings much easier to observe during testing. The oil-based material, however, never completely dried and could not be touched even at low temperatures. Despite this, it was the material of choice for the final evaluation.

3.1.3 Heating Method

Screening tests were originally done by merely placing the cartridge cases base down on a laboratory hot plate. The temperature of the hot plate was regulated by an auto transformer (Variac). Once LC materials had been chosen, it was necessary to design a better regulated method of heating the cartridge case.

We constructed the apparatus shown in Figure 2, it is a 3/4-in. square brass bar 6 in. long. Construction details are shown in Figure 3. A half-round groove in the bottom accommodates a tubular 100 watt heating element controlled by a Variac. The temperature of the bar, just below its upper face, is sensed by three thermocouples located as indicated and connected to a strip chart recorder. In operation, the temperatures indicated by these couples were within $\pm 2^{\circ}$. This in turn assured that the heat flux applied to cases on the bar would be uniform. Six locations were spotfaced about 1/16-in. deep, as shown, at a diameter only slightly larger than the base of a 5.56 mm case. This provided for uniform location and contact between the heat source and the case.

The entire unit rested on a piece of heavy asbestos tape on top of a silica fire brick. When in use, the assembly was located in a small open top box with three small windows in front for lighting and viewing. The box protected against air currents disturbing the heating of the cases.

At the start of the test the bar was heated to the desired temperature by adjusting the Variac until the temperature was constant. The sample cases were placed in the spot-faced location as shown and the progression of the color rings observed.



Figure 2

Heating Apparatus for the Liquid Crystal Test

Incandescent lighting was provided, making the colors more apparent than under fluorescent illumination. Reflections were a problem on the curved surface of the case, particularly at the shoulder and neck transitions. The use of polarizing filters to reduce these reflections was of marginal benefit.

At the conclusion of the test, the cases were removed, the bar temperature allowed to equilibrate, and the procedure repeated.

Three bar temperatures were chosen. At the lower temperature, about 60°C, the color ring was about 5/16 in. wide, (red on top, violet on the bottom) and traversed the case from base to mouth in about 15 to 20 seconds, depending on the LC used. At a bar temperature of 75°C, the ring was 1/4 in. high and travelled in only about 12 sec. The highest temperature of 112-116°C had a 3/16 in. high color band and took 8-10 seconds.

3.2 Observations and Data

One hundred each of A and NA 5.56 mm cartridge cases had been obtained from LCAA. These were coded by light file marks on the base as (A) or (NA), degreased, and black-coated. They were coated as needed with the appropriate LC by spraying or brushing.

The objective was to determine any observable differences between A and NA cases. Thus an A and an NA case coated with the same LC formulation would be placed on the bar at the same time and the results observed. This was done with both the LIX and Djinni LC having color transition temperatures of 30, 32, 33°C.

A comparison of A cases side by side with NA cases showed no consistent observable pattern of difference in the moving color rings.

Since this effect occurred in 10 to 20 seconds, an attempt was made to film the tests with an 8 mm movie camera, so that the behavior could later be examined at a slower rate. This proved to be very difficult. The intense light necessary to get high quality films heated the cases and washed out the "ring effect." At low levels of light the color contrast was not sufficient to register well.

Thus, whether the bullets were left in or removed from the case, one could not detect any repeatable difference in color or pattern to indicate whether or not the case mouth had been properly annealed.

These observations and conclusions were very subjective, as they depended on visual observation to detect differences in the size or pattern of the color rings produced by A or NA 5.56 mm cases. The observations were made under the experimental conditions and with the materials indicated in Table 1.

The time interval during which the red band first touched the shoulder of the case and the last blue violet color disappeared from the case neck was recorded for both A and NA samples. This was done with the bullet in place to act as a heat sink. A difference in thermal conductivity might register as the time to transfer an amount of heat equivalent to the 2-3°C temperature span from the case body to the bullet.

Typical data are shown in Table 2. (Even-numbered tests are A cases, odd-numbered tests are NA cases.) The data, however, does not give clear evidence of any differences between the tests. Accordingly, Students "t test" on the average of two means was applied to examine the probability of stating that there was or was not a difference. Typical data are shown in Table 3. If the calculated value of t is larger than 2.30 (for 8 samples, i.e., $n_1 + n_2 - 2$), one can state at the 95% confidence level, that the compared groups have a different mean, i.e., were drawn from a different population.

Table 1

Experimental Matrix for the Evaluation of
Liquid Crystal Thermography

		LIQUID CRYSTAL SOURCE			
		LIX KIT		DJINNI	
TRANSITION TEMP. °C		32	33	30	32
Heating	63	10	10	10	10
Block	76	10	10	10	10
Temp °C	112	10	10	10	10

Ten cases, 5 annealed and 5 not annealed, were compared side by side (2 at a time) for each of the experimental conditions shown.

Table 2

Time (sec) Required For the Color Ring to Pass Completely
From the Case Shoulder Through the Case Mouth

HEATING BLOCK TEMP. (°C)	TEST NO.			
	1	2	3	4
63°	10	10	16	11
	17	13	17	13
	16	16	12	16
	15	15	14	14
76°	TEST NO.			
	5	6	7	8
	13	11	8	11
	14	13	10	11
	16	12	11	12
	15	13	11	12
112°	14	13	12	11
	TEST NO.			
	9	10	11	12
	10	8	9	9
	10	9	8	8
	12	8	8	11
	11	10	11	11
	12	9	11	12

¹Odd-Numbered Tests were on Not Annealed Cases
Even-Numbered Tests were on Annealed Cases

Table 3

Students "t test" on Two Means For Typical Time Data of Table 2

	TEST NO.				TEST NO.			
	1	2	3	4	9	10	11	12
\bar{x}	12.8	11.2	12.8	11.8	11.0	8.8	9.4	10.2
$\Sigma'X$	86.8	46.8	50.8	70.8	4.0	2.8	9.2	10.8
n	5	5	5	5	5	5	5	5
s(x)	4.7	3.4	3.6	4.2	1.0	0.84	1.52	1.64

Comparing Tests	t	Comparing Tests	t
1 vs 3	0.00	9 vs 11	1.97
2 vs 4	0.25	10 vs 12	1.70
1 vs 2	0.54	9 vs 10	3.78
1 vs 4	0.36	9 vs 12	0.93
3 vs 2	0.72	11 vs 10	0.77
3 vs 4	0.41	11 vs 12	0.80

The intent is to test the hypothesis that the samples have the same means, i.e., that they are from the same population. At the 95% confidence level the hypothesis can be rejected only when $t > 2.30$ for 8 degrees of freedom ($n-2$). The above tables indicate that all cases were drawn from the same population, though in fact all odd-numbered tests (not annealed) cases are different from even-numbered (annealed) samples.

The data clearly indicate, as far as this test procedure is concerned, that one cannot distinguish between A and NA 5.56 mm cartridge cases.

If the effect is dependent upon differences in the heat capacity and/or thermal conductivity of A versus NA cases, this could be produced another way.

A #80 drill was used to put a hole in the side of a case. When the drilled case was placed on a hot plate, the presence of the hole could not be discerned as any kind of dislocation or warping in the color bands as they passed its vicinity. Yet such a hole certainly represents a gross local difference in heat capacity.

A small drop of solder was melted onto the inside of the neck of a cartridge case. Again no discernable difference in the LC patterns was discernable compared to an untreated case.

These tests, along with the comparisons made between A and NA cases, indicate there is no hope that this procedure could replace the mercury cracking test as a quality assurance procedure.

4. CONCLUSIONS AND RECOMMENDATIONS

The observations made during the course of this program offer no hope of using LC to detect improper annealing of brass cartridge cases. Such a test would be effective only if the differences in heat capacity and thermal resistance between the A and NA crystal structures were sufficient to cause a difference of several degrees in the surface temperature of the cartridge case. While a difference in thermal properties might exist, it certainly is not as large as the difference due to a hole (the #80 drill) or the drop of solder.

The problem is also biased by random error resulting from the application of a black undercoat of some finite thickness, which tends to "smear" any observable effect. The difficulty

of uniformly applying the LC coating is a similarly confounding factor.

In many other applications, in a sense similar to this, the sought after defect is continuously hotter say, than its surroundings and observable almost at will, e.g., electronic parts or physiological differences. Here any effect while smaller must be observed "on the fly."

There seems to be no merit in further pursuing the application of LC to this problem. This is not to say that the problem of disposing of waste mercury and acid solutions should not be treated.

Further, in viewing the Small Caliber Ammunition Modernization Plant (SCAMP) lines in operation at LCAAP one is impressed with the desirability of a much quicker quality control test. The mercury cracking test requires more than half an hour to gather the samples and get an answer. In the interval, thousands of cartridge cases have been made by one production line.

Two alternative tests may merit investigation. One test, based on eddy currents, operates on differences in resistance between the A and NA metals, and we understand was being considered by Frankford Arsenal.

The other test, based on the difference in x-ray diffraction patterns between the two states, could be an almost instant in-line quality control technique. Captured on a video display or magnetic tape, computer-aided pattern recognition techniques could answer the question of proper annealing.

APPENDIX

ASTM B 154-73

MERCUROUS NITRATE TEST FOR COPPER AND COPPER ALLOYS



Standard Method of MERCUROUS NITRATE TEST FOR COPPER AND COPPER ALLOYS¹

This Standard is issued under the fixed designation B 154; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

This method has been approved for use by agencies of the Department of Defense to replace method 831 of Federal Test Method Standard No. 1516 and for listing in the DoD Index of Specifications and Standards.

NOTE 1: Caution—Mercury is a definite health hazard in use and disposal (Notes 4 and 6 and Section 4).

1. Scope

1.1 This method describes the technique for conducting the mercurous nitrate test of commercial wrought copper and cast or wrought copper-base alloy products. This is an accelerated test for the purpose of detecting in copper or copper-base alloy products the presence of residual (internal) stresses that might bring about failure of the material in service or storage through stress-corrosion cracking. This method is intended to cover the mercurous nitrate test of certain copper-alloy products supplied in accordance with ASTM specifications prepared by Committee B-5. If it is used for testing assemblies and fabricated parts, failure shall not be cause for rejection of the original mill product.

NOTE 2—For any particular copper alloy, reference should be made to the material specification.

NOTE 3—The values stated in U.S. customary units are to be regarded as the standard.

2. Definitions

2.1 The following definitions are included for information:

2.1.1 *stress corrosion crack*—spontaneous failure of metals by cracking under combined action of corrosion and stress, residual or applied.

2.1.2 *residual stress*—stresses that remain within a body as the result of plastic

deformation or casting.

3. Mercurous Nitrate Solution

3.1 *Concentration*—The solution shall be an aqueous mercurous nitrate solution containing 10 g of HgNO_3 and 10 ml of HNO_3 (sp gr 1.42) per liter of solution.

3.2 *Preparation*—The aqueous mercurous nitrate solution shall be prepared by either of the following procedures A or B. Used solutions may be replenished as described in 3.3.

3.2.1 *Procedure A*—Dissolve 11.4 g of $\text{HgNO}_3 \cdot 2\text{H}_2\text{O}$ or 10.7 g of $\text{HgNO}_3 \cdot \text{H}_2\text{O}$ in approximately 40 ml of distilled water acidified with 10 ml of HNO_3 (sp gr 1.42). After the crystals are completely dissolved, dilute the solution with distilled water to 1000 ml.

NOTE 4—The mercurous nitrate crystals are obtainable in both the monohydrate and dihydrate form and should be handled with caution because of their highly toxic effects. When weighing crystals, the weight of the water of crystallization should be taken into consideration. The mercurous nitrate crystals are photosensitive and when they have turned yellow are difficult to dissolve.

3.2.2 *Procedure B*—Dissolve 76 g of mercury in 114 ml of diluted HNO_3 (1 part water to 1 part HNO_3) (sp gr 1.42). Carefully dilute with distilled water to 1000 ml. This provides a concentration of 100 g of

¹ This method is under the jurisdiction of ASTM Committee B-5 on Copper and Copper Alloys.

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HNO₃ after a slight loss due to heating. Add the water in small portions while stirring to prevent local overdilution. This gradual dilution, together with the excess acid, will prevent precipitation of basic salts of mercury. Dilute 100 ml of this solution (10 percent) with 7 ml of HNO₃ (sp gr 1.42) and 893 ml of water.

NOTE 5—If heating is used in either of these procedures for preparing the mercurous nitrate solution, care should be exercised to avoid loss of HNO₃.

3.3 *Replenishment of Solution*—The spent solution may be reclaimed by replenishing the mercurous nitrate solution, to a 1 percent concentration, as follows:

3.3.1 Measure as accurately as possible in a small graduated cylinder 50 ml of the spent HgNO₃ solution.

3.3.2 Transfer to an Erlenmeyer flask, and add 10 ml of HNO₃ (1+1).

3.3.3 Add slowly KMnO₄ solution (1 percent) from a buret with a constant shaking until there is an excess as indicated by the pink color, which persists for several minutes.

3.3.4 Add FeSO₄ crystals until the solution, when shaken, becomes clear. Then titrate the solution with 0.1 N KCNS solution to the appearance of a reddish brown color. Repeat this procedure with 50 ml of a standard HgNO₃ solution (1 percent).

3.3.5 The ratio, *R*, of the number of milliliters of KCNS solution required to titrate the spent solution, to the number of milliliters required to titrate the standard solution, determines the number of milliliters, *X*, of 10 percent HgNO₃ in 3 percent HNO₃ solution required to replenish 1 liter of spent solution. Values of *R* and *X* for a liter volume are given in Table I.

4. Safety Precautions

4.1 CAUTION—Mercury is a definite health hazard in use and disposal.

4.2 *Suggested Mercurous Nitrate Disposal:*

4.2.1 To mercurous nitrate solutions add sodium hydroxide to pH 10–11.

4.2.2 Filter precipitated mercury and other heavy metals.

4.2.3 Though the filtrate is low in free mercurous or mercuric ions, it must be further

treated before disposal.

4.2.4 To each litre of filtrate, add two drops (0.1 cm³) of 24 % ammonium sulfide.

4.2.5 After the second filtering, the filtrate may be discarded.

4.2.6 The precipitates should be collected and stored with the mercury contaminated test samples and sold to a metal reclaimer.

5. Test Specimen

5.1 The test specimen shall be of the size prescribed in the specification for the material being tested. To obtain the most significant test on rod, wire, and tube, it is recommended that, in the absence of a prescribed specimen size in the product specification, the test specimen be at least 6 in. (152 mm) in length or twice the diameter, whichever is greater, when practicable.

6. Procedure

6.1 Degrease the specimen in a suitable alkaline degreasing solution or organic solvent. If necessary, totally immerse the specimen in an aqueous solution of sulfuric acid (15 volume percent) or nitric acid (40 volume percent) until all oxides are completely removed from its surface or pickle in such solutions as may be prescribed in the specification for the material being tested. Remove the specimen from the pickling solution and wash it immediately in running water. Then drain the specimen free of excess water and totally immerse it at room temperature in the mercurous nitrate solution prepared in accordance with 3.2. Use at least 10 ml of mercurous nitrate solution per square inch of exposed surface of the test specimen.

6.2 After 30 min remove the specimen from the mercurous nitrate solution and wash it in running water. Wipe off any excess mercury from the surface of the specimen. Immediately examine it visually for cracks unless a time limitation is provided in the product specification. In cases of doubt regarding the presence of cracks, volatilize (Caution, Section 4 and Note 6) the mercury on the surface of the specimen by the application of heat on a hot plate or in an oven. Then examine the specimen for cracks under suitable magnifying equipment at a

magnification of 10 to 18 diameters.

6.3 Do not reuse the solution unless it is replenished to 1 percent in accordance with the procedure in 3.3.

NOTE 6: Caution—Mercury is a definite health hazard and therefore equipment for the detection and removal of mercury vapor produced in volatilization is recommended. The use of rubber gloves in testing is advisable.

TABLE 1 Replenishment of Spent Mercurous Nitrate Solution to 1 Percent Concentration

NOTE— $X = 111.1(1 - R)$

where: R = fraction of mercury remaining in solution (determined by titration), and

X = number of milliliters of mercurous nitrate solution (10 percent) to be added to 1 liter of spent mercurous nitrate solution to raise the concentration of mercurous nitrate to 1 percent.

R	X	R	X
0.10	100.0	0.56	48.9
0.12	97.8	0.58	46.7
0.14	95.5	0.60	44.4
0.16	93.3	0.62	42.2
0.18	91.1	0.64	40.0
0.20	88.9	0.66	37.8
0.22	86.7	0.68	35.6
0.24	84.4	0.70	33.3
0.26	82.2	0.72	31.1
0.28	80.0	0.74	28.9
0.30	77.8	0.76	26.7
0.32	75.5	0.78	24.4
0.34	73.3	0.80	22.2
0.36	71.1	0.82	20.0
0.38	68.9	0.84	17.8
0.40	66.7	0.86	15.6
0.42	64.4	0.88	13.3
0.44	62.2	0.90	11.1
0.46	60.0	0.92	8.9
0.48	57.8	0.94	6.7
0.50	55.6	0.96	4.4
0.52	53.3	0.98	2.2
0.54	51.1		

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